

Appendix E

Iterative Divergent/Convergent Doubling Approach to Linear Conjugated Oligomers. A Rapid Route to a 128 Å Long Potential Molecular Wire

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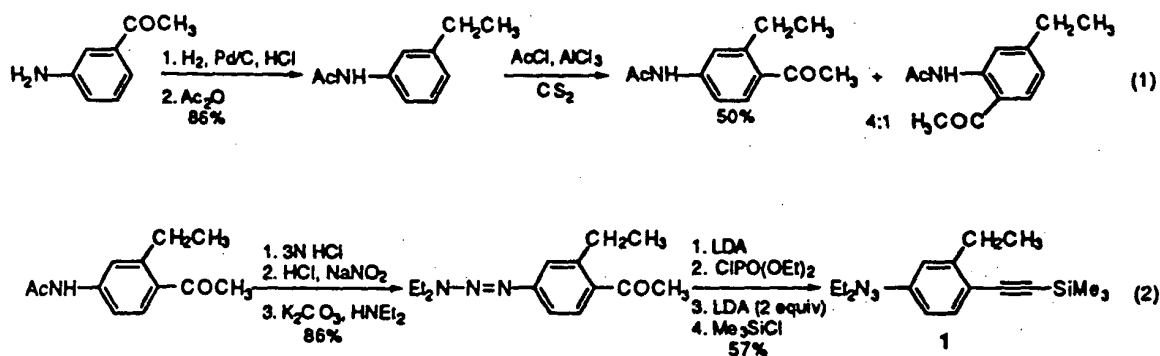
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Abstract

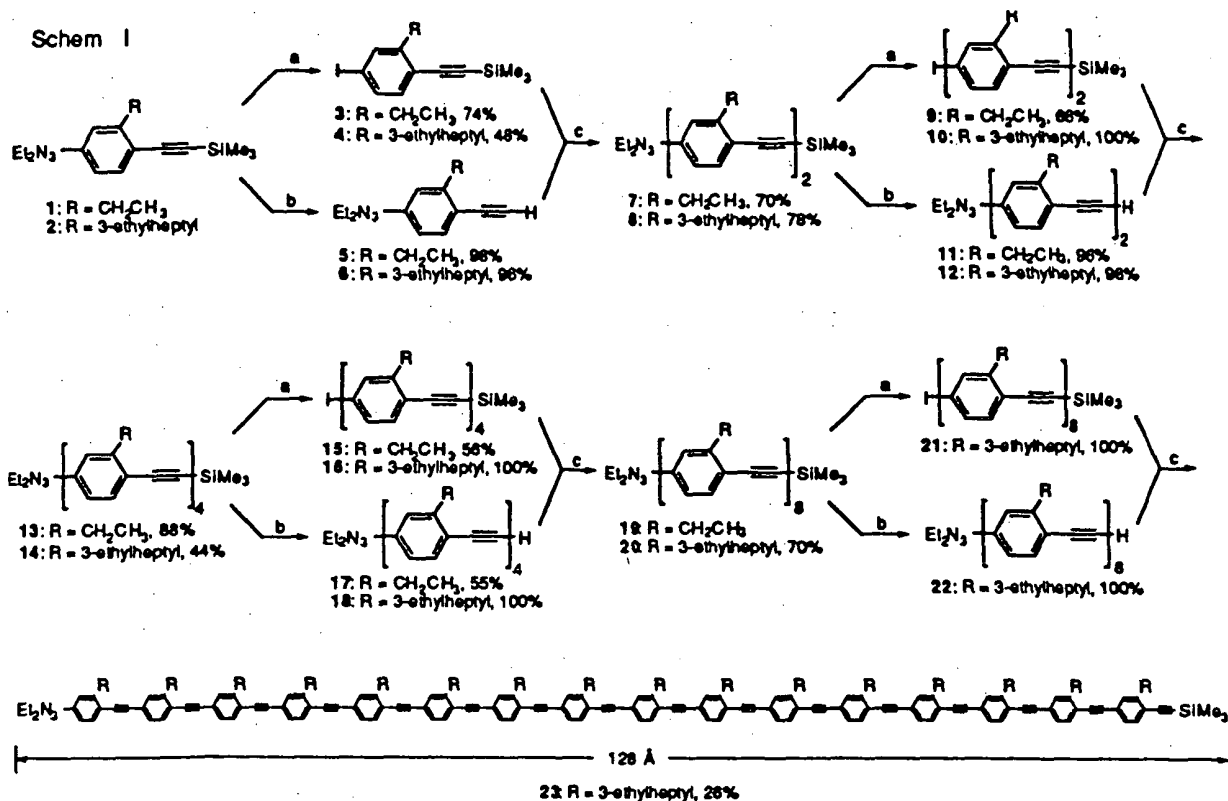
Described is the synthesis of oligo(2-ethylphenyl-ethynylene)s and oligo(2-(3'-ethylheptyl)phenyl-ethynylene)s via an iterative divergent convergent approach. Synthesized were the monomer, dimer, tetramer, and octamer of the ethyl derivative and the monomer, dimer, tetramer, octamer, and 16-mer of the ethylheptyl derivative. The 16-mer is 128 Å long. At each stage in the iteration, the length of the framework doubles. Only three sets of reaction conditions are needed for the entire iterative synthetic sequence; an iodination, a protodesilylation, and a Pd/Cu-catalyzed cross coupling. The oligomers were characterized spectroscopically and by mass spectrometry. The optical properties are presented which show the stage of optical absorbance saturation. The size exclusion chromatography values for the number average weights, relative to polystyrene, illustrate the tremendous differences in the hydrodynamic volume of these rigid rod oligomers verses the random coils of polystyrene. These differences become quite apparent at the octamer stage. A plot of the actual molecular weights versus size exclusion chromatography-determined molecular weights for these linear oligomers are similar to the plots obtained for other rigid rod oligomers; therefore confirming that such plots are superbly suited for molecular weight determination of rigid rod polymers. These oligomers may act as molecular wires in molecular electronic devices and they also serve as useful models for understanding related bulk polymers.

The ultimate computational system would consist of logic devices that are ultra dense, ultra fast, and molecular-sized.¹ Even though state-of-the-art nanopatterning techniques allow lithographic probe assemblies to be engineered down to the 100 Å gap regime,² the issue of electronic conduction based upon single or small packets of molecules has not been demonstrated and the feasibility of molecular electronics remains theoretically controversial.^{1,3} In an attempt to assess the possibility of molecular wire conduction by spanning the 100 Å probe gaps with molecules, we recently described a new rapid synthetic approach to potential molecular wires based on an oligo(thiophene-ethynylene) derivative.^{4,5} Those thiophene-ethynylene-derived compounds existed in a zig-zag conformation due to the 148° bond angle across thiophenes. Complementary to that, we describe here the synthesis of phenylene-alkynylene oligomers that remain in a linear conformation. This linear arrangement should minimize undesired conformational movement during adhesion and testing between nanofabricated probes. Our approach to such a molecular framework involves a rapid iterative method that doubles molecular length at each iteration to provide an air and light-stable linear conjugated oligomer that is 128 Å long that could also serve as a useful model for understanding bulk polymeric material properties.⁶ Moreover, the product could easily permit independent functionalization of the ends to serve as "molecular alligator clips" that might be required for surface contacts to metal probes.⁷

The synthesis of the ethyl-containing monomer **1** is shown in eqs 1 and 2. The iterative



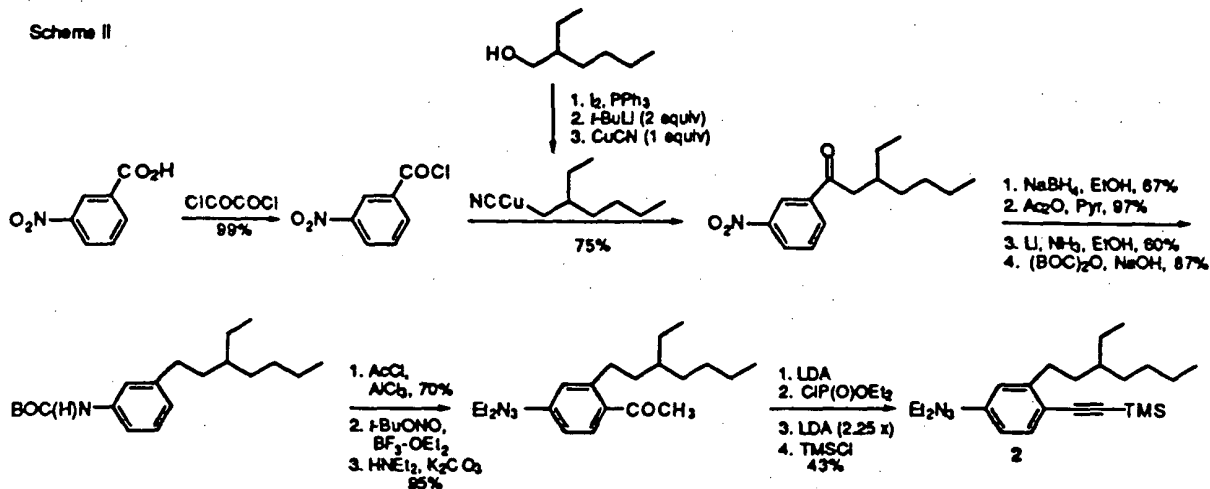
divergent/convergent approach to molecular length doubling is shown Scheme I. Notice how just three different reactions are needed at each stage to double the molecular length.⁸ We initially



Reagents: a. MeI as solvent, 120°C in a screw cap tube. b. K₂CO₃, MeOH, 23°C or n-Bu₄NF, THF, 23°C c. Pd(dba)₂ (5 mol %), CuI (10 mol %), PPh₃ (20 mol %), iPr₂NH/THF (1:5), 23°C.

conducted the synthesis starting from the monomer 1 with the notion that the ethyl group would provide sufficient solubility to permit formation of a 16-mer that has a length sufficiently long to bridge between lithographically-derived probe gaps. Unfortunately, the octamer 19 was nearly insoluble. We were only able to obtain a UV-visible spectrum (λ_{max} (CH₂Cl₂) = 364 nm) and a mass spectrum (MS). Further analysis and synthesis was prohibited due to the poor solubility.

In an effort to insure the solubility of the linear rigid rod oligomer through to the 16-mer, we prepared the monomer 2 as shown in Scheme II. We tried numerous methods to concomitantly reduce both the ketone and the nitro moiety, however, all methods failed, including the Pd-C/H₂/HCl reduction that worked for in the synthesis of 1 (eq 1 and 2). Therefore the multi-step reaction sequence shown in Scheme II had to be utilized which also required a *tert*-BuONO-promoted⁹ formation of the intermediate diazonium species. In addition to 2 possessing a longer alkyl chain than 1, 2 also has a stereogenic center which, upon successive dimerization, will afford numerous



diastereomers that will retard crystallization and thereby increase the likelihood of solubility. Indeed, we were delighted to discover that both the octamer 20 as well as the 16-mer 23 (Scheme I) were quite soluble and they could be fully characterization.

While 1, 2, 7, 8, 13, and 14 afforded molecular ions by direct exposure via electron impact mass spectrometry (MS), 19 exhibited a peak for its molecular weight minus the triazene group that was lost during MS analysis. In order to characterize 20 and 23, it was necessary to use matrix assisted laser desorption MS to observe their respective $M+1$ peaks (Calc'd maximum isotopic intensity for 23, with $X^{13}\text{C } M+1 = \text{XXXX}$. Found $\text{XXXX} \pm \text{XX}$).

The optical spectra are interesting in that a saturation of the systems appears to have occurred by the octamer stage so that doubling the conjugation length to the 16-mer caused little change in the absorbance maximum (Figure 1). We also noticed that the π -extended triazene substituent shifted the absorbance maxima bathochromically.

The results of the size exclusion chromatography (SEC) are shown Figure 2 as compared with the actual molecular weights (MW) of the oligomers. SEC is not a direct measure of MW but a measure of the hydrodynamic volume. Thus, by SEC using randomly coiled polystyrene standards, the number average molecular weights (M_n) of rigid rod polymers are usually greatly inflated relative the actual molecular weights. Accordingly, the SEC recorded M_n values of the octamer (20) ($M_n = 2,790$, actual MW = 1,981) and 16-mer (23) ($M_n = 6,650$, actual MW = 3,789) were much greater than the actual MWs. Conversely, the monomer (2) through tetramer

(14) had M_n values that were reasonably close to the actual MWs (slope ~ 1.0 in Figure 2) because they are in the low MW region, prior to significant polystyrene coiling. In all cases, the SEC-determined values of $M_w/M_n = 1.04$ -1.07. Remarkably, as also demonstrated in Figure 2, the curve is quite similar to the thiophene-ethynylene-derived oligomers⁴ that possess a zig-zag conformation, thus substantiating that Figure 2 could serve as a useful calibration chart for estimating the MWs of various other rigid rod polymers.

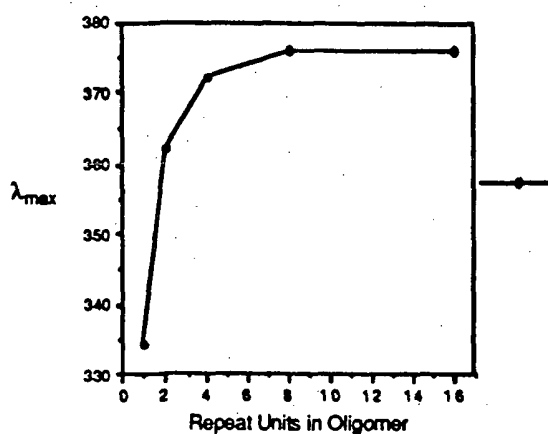


Figure 1. UV absorbance maxima (CH_2Cl_2) of the monomer through 16-mer, 2, 8, 14, 20, and 23, respectively.

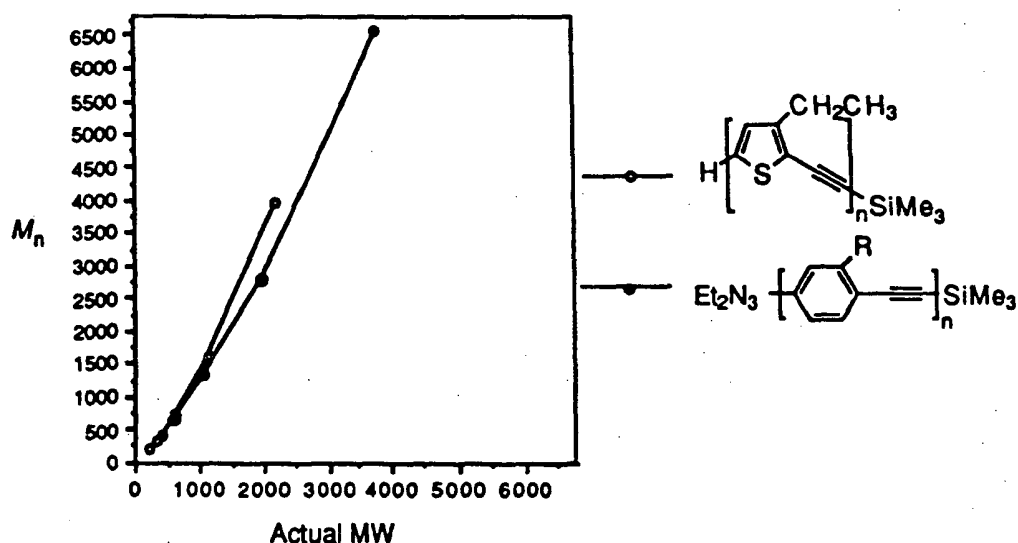


Figure 2. M_n as determined using SEC (THF, polystyrene) versus the actual molecular weights of the two oligomers shown where $n = 1, 2, 4, 8$, and 16. $R = 3$ -ethylheptyl.

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References

- (1) (a) Bowden, M. J. In *Electronic and Photonic Applications of Polymers*; Bowden, M. J.; Turner, S. R., Eds.; (Advances in Chemistry, 218) American Chemical Society: Washington DC, 1988. (b) *Molecular Electronics: Science and Technology*, Aviram, A., Ed.; Confer. Proc. No. 262, American Institute of Physics: New York, 1992. (c) *Molecular Electronic Devices II*; Carter, F. L., Ed.; Marcel Dekker: New York, 1984. (d) Hammeroff, S. R. *Ultimate Computing. Biomolecular Consciousness and Nano Technology*; North Holland: Amsterdam, 1987. (e) Franks, A. *J. Phys. E: Sci Instrum.* 1987, 20, 1442. (f) Miller, J. S. *Adv. Mater.* 1990, 2, 495, 601. (g) Aviram, A. *J. Am. Chem. Soc.* 1988, 110, 5687. (h) Hush, N. S.; Wong, A. T.; Bacskay, G. B.; Reimers, J. R. *J. Am. Chem. Soc.* 1990, 112, 4192. (i) Farazdel, A.; Dupuis, M.; Clementi, E.; Aviram, A. *J. Am. Chem. Soc.* 1990, 112, 4206. (j) Waldeck, D. H.; Beratan, D. N. *Science* 1993, 261, 576. (k) Ball, P.; Garwin, L. *Nature* 1992, 355, 761. (l) Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* 1990, 112, 5662.
- (2) (a) Reed, M. A., Yale University, personal communication, 1993. (b) *Nanostructure Physics and Fabrication*, Reed, M. A.; Kirk, W. P., Eds.; Academic Press: San Diego, 1989. (c) *Nanostructures and Mesoscopic Systems*, Kirk, W. P.; Reed, M. A., Eds.; Academic: San Diego, 1992.
- (3) (a) Miller, J. S. *Adv. Mater.* 1990, 2, 378. (b) Chjatterji, P. K.; Yang, P. Schichijo, H. *Proc. IEEE* 1983, 130, 105. (c) Bate, R. T. In *VSLI Electronics*, Einspruch, N. G., Ed.; Academic: San Diego, 1982; Vol 5.
- (4) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *J. Am. Chem. Soc.*, under review.

(5) For a presentation of some foundational work in the area, see: (a) Kenny, P. W.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* 1988, 85. (b) Kugimiya, S.-i.; Lazrak, T.; Blanchard-Desce, M.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* 1991, 1179. (c) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* 1991, 1569. (d) Zecevic, S. ### *J. Electroanal. Chem.* 1985, 196, 339. (e) Yoshimura, T.; Tatsuura, S.; Sotoyama, W.; Matsuura, A.; Hayano, T. *Appl. Phys. Lett.* 1992, 60, 268. (f) Sessler, J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* 1993, 115, 4618. (g) Tachibana, H.; Azumi, R.; Nakamura, T.; Matsumoto, M.; Kawabata, Y. *Chem. Lett.* 1992, 173. (h) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L., III; Wasielewski, M. R. *Science* 1992, 257, 63.

(6) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986.

(7) (a) Abbott, N. L.; Folkers, J. P.; Whitesides, G. M. *Science* 1992, 257, 1380. (b) Charych, D. H.; Bednarski, M. D. *Mater. Res. Soc. Bull.* 1992, 17(11), 61.

(8) For the iodination procedure, see: Moore, J. S.; Weinstein, E. J.; Wu, Z. *Tetrahedron Lett.* 1991, 32, 2465. For the cross coupling procedure, see: (a) Kumada, M.; Suzuki, K.; Tamao, K.; Kodama, S.; Nakajima, I.; Minato, A.; *Tetrahedron* 1982, 38, 3347. (b) Uhlenbroek, J. H.; Bijloo, J. D. *Rec. Trav. Chim.* 1960, 79, 1181. (c) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* 1975, 4467. (d) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* 1963, 28, 3313. (e) Suffert, J.; Ziessel, R. *Tetrahedron Lett.* 1991, 32, 757.

(9) Doyle, M. P.; Bryker, W. J. *J. Org. Chem.* 1979, 44, 1572.